Prediction of Contaminant Retention and Transport in Soils Using Kinetic Multireaction Models

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Mathematical models that describe the retention reactions of contaminants in the soil system are presented. Single and multireaction-type models for simultaneous retention and transport in the soil profile are discussed. Single retention models are classified into two types: equilibrium and kinetic models. Emphasis is given to the nonlinearity and kinetic behavior of solute retention processes in soils. Two-site models that include the equilibrium-kinetic types as well as the fully kinetic type are also examined. A multireaction-type model is also presented, which includes reversible and irreversible retention processes of the equilibrium and kinetic types. Advantages of the multireaction approach over the single or two-site models are discussed. The predictive capability of the two-site model and the multireaction model for their description of experimental results for phosphorus and two heavy metals (Cd and Cr) are examined.

Introduction

Retention reactions that occur in the soil are important processes that govern the fate of chemical contaminants and hazardous chemicals in groundwater. Mathematical models that describe the potential mobility of dissolved chemicals must therefore include the physical and chemical, as well as biological, processes that influence the behavior of these chemicals in the soil matrix. The ability to predict the mobility of dissolved chemicals in the soil and the potential contamination of groundwater supplies is important in assessment of hazards and is a prerequisite for the management of land disposal of chemicals contaminants.

In this paper, a review of widely used solute retention models is presented. Emphasis is on solute retention mechanisms characterized by time-dependent (or kinetic) and nonlinear type reactions. Several multireaction models for the transport and retention of contaminants are presented.

Equilibrium Retention Models

It is well accepted that, under steady water flow conditions, transport of dissolved chemicals in soils is governed by the following convection-dispersion transport equation (1):

$$\rho \frac{\partial s}{\partial t} + \Theta \frac{\partial c}{\partial t} = \Theta D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} - Q \qquad (1)$$

where c is the concentration of the dissolved chemical in the soil solution (mg/L) and s is the amount of solute retained per unit mass of the soil matrix (mg/kg). In addition, D is the hydrodynamic dispersion coefficient (cm^2/day), q is the Darcy water flux (cm/day), Θ is the volumetric soil moisture content (cm^3/cm^3), ρ is the soil bulk density (g/cm^3/day), t is time (day) and x is soil depth (cm). The two terms on the right-hand side of Eq. (1) are commonly known as the dispersion and convection terms, respectively. The term $(\partial s/\partial t)$ represents the rate for reversible solute removal from the soil solution. In contrast, the term Q is a source or a sink representing irreversible solute production (Q negative) or solute removal (Q positive) from the soil solution ($mg/cm^3 \cdot$ day).

Over the last 2 decades, several analytical models for the description of solute transport in porous media have been proposed. One group of models deals with solute transport in well-defined geometrical systems of pores and/or cracks of regular shapes or interaggregate voids of known geometries. Examples of such models include those of Rao et al. (2), Rasmuson and Neretnieks (3) (for uniform spheres), Tang et al. (4) (for rectangular voids), van Genuchten et al. (5) (for cylindrical voids), and Rasmuson (6) (for discrete aggregate or spherical size geometries). van Genuchten and Dalton (7) provided a review of models using such an approach. Solutions of these models are analytic, often complicated, and involve several numerical approximating steps. Recent applications include transport in fixed beds consisting of spheres or aggregates (8,9). Another group of transport models that are widely used are those that do not consider well-defined geometries of the pore

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space or soil aggregates. Rather, solute transport is treated on a macroscopic basis with ρ, θ, q, and D of Eq. (1) as the associated parameters that describe the transport processes in the bulk soil. The mobile-immobile transport models are refinements of this macroscopic approach. Here, it is assumed that soil-water is divided into two regions. A mobile-water region is one that is considered to be present in large pores and through which solute transport occurs by convection and mechanical dispersion. The other is an immobile-water region present in the bulk matrix and through which relatively low or no water flows. Mobile-immobile models have been introduced by Coats and Smith (10), Skopp and Warrick (11), van Genuchten and Wierenga (12), and Skopp et al. (13). The mobile-immobile models have been extensively used to describe several solutes [for a review see Nielsen et al. (14)].

Description of the solute retention mechanisms as expressed by the term $(\partial s/\partial t)$ has been the focus of investigators for several years. Such a description, when incorporated into Eq. (1), provides a predictive tool for the transport of dissolved chemicals in the soil profile. Most mathematical models that describe the retention mechanisms are based on the validity of the local equilibrium assumption (LEA) in the soil system (15). Here one assumes that the reaction of an individual solute species in the soil is sufficiently fast or instantaneous and that an apparent equilibrium condition may be observed in a few minutes or hours. Such a behavior has been used as the basis for soil surface adsorption mechanisms as well as ion-exchange reactions. Illustrative examples of equilibrium-type solute retention are shown in Figure 1. The data are from kinetic batch experiments of Mg retention by a Ca saturated Abist soil and for two aggregate size separates. The time of reaction does not appear to be significant. No apparent change in Mg concentration occurred after 4 hr of reaction. Such rapid retention reactions or equilibrium solute behavior has been observed for other solutes (16-18).

Linear, Freundlich, and Langmuir sorption models are perhaps the most commonly used equilibrium-type models for describing the retention of a wide range of dissolved chemicals in soils. A partial listing of equilibrium type models are given in Table 1. The linear and Freundlich models use the solute distribution coefficient (K_D), which partitions the solute between that in the soil solution and the amount sorbed by the soil matrix. A discussion of the K_D parameter and its capability for describing contaminant migration is given by Reardon (19). Unlike the Langmuir models, linear and Freundlich models do not include a maximum sorption term (s_{max}). This is disadvantageous since the capacity of the soil for solute removal, i.e., the total sites, is finite and should be an important limiting factor.

Langmuir models are perhaps the most widely used equilibrium models for describing the fate of solutes such as phosphorus and heavy metals in soil (18,20,21). The two-site Langmuir model may be considered as one of the earliest multireaction type models. Here one as-
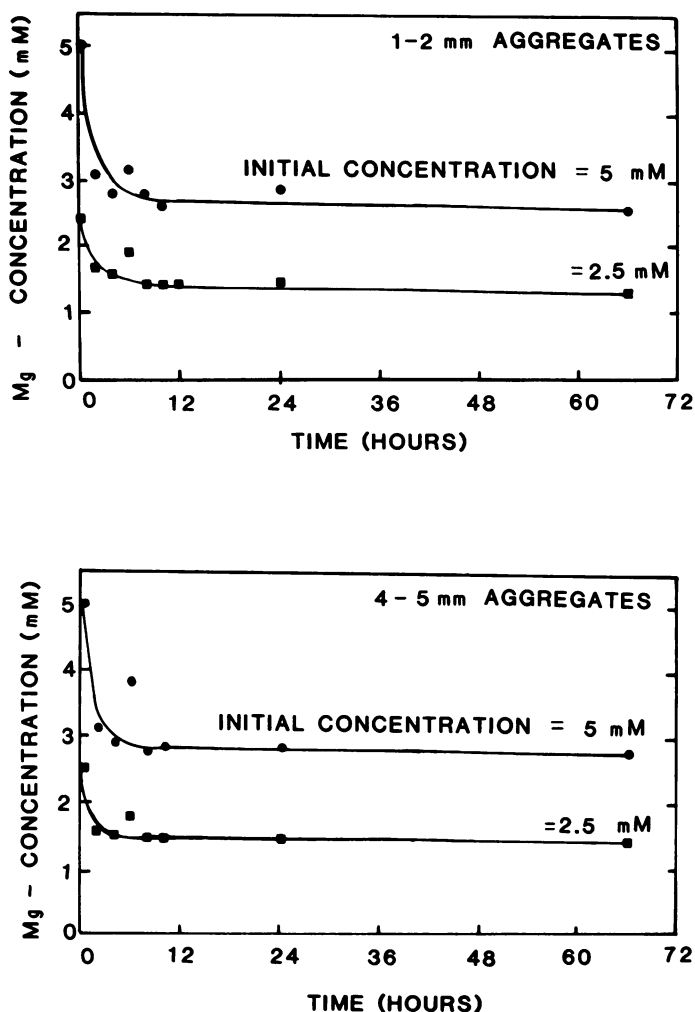

FIGURE 1. Mg concentration vs. time of reaction from batch kinetic experiments for two aggregate sizes of Abist (Aquic Eutrochrept) soil (15).

Table 1. Fast or equilibrium type models for contaminant retention in soils.

Model	Formulation
Linear	$s = K_D c$
Freundlich (nonlinear)	$s = K_D c^n$
Langmuir	$s = bc s_{max}/[1 + bc]$
Langmuir with sigmoidicity	$s = bc s_{max}/[1 + bc + k/c]$

sumes complete equilibrium and partitions the reaction sites into two fractions. Holford et al. (22) were one of the earliest researchers to evaluate this model for describing P retention by several soils.

Recently, the two-site Langmuir was modified to incorporate the sigmoidal shape of Cu, Pb, and Cd sorption isotherms observed at extremely low concentrations (23). The equilibrium models given in Table 1 have been used to describe adsorption isotherms for a wide range of solutes including major cations (Na, Ca, Mg, and K), heavy metal species, and organics (16,24). How-

ever, as pointed out by Veith and Sposito (25) and Sposito (26), a good fit of a particular adsorption isotherm does not in itself constitute a proof of any specific sorption mechanism.

Other types of equilibrium models are those based on ion-exchange reactions (27,28). Unlike the previous models, which are empirical in nature, ion-exchange models are based on rigorous thermodynamics in which the reaction stochiometry is explicitly considered. A set of recursion formulae has been formulated by Rubin and James (27) that describe exchange isotherms for multiple ions in the soil. Recently, aqueous equilibrium reactions, along with ion-exchange reactions, have been used to describe multiple ion transport in soils (29,30). Ion exchange has been used by several researchers to describe the transport of cations present in the soil solution (28,31–33).

Kinetic Retention Models

It has been observed that the amount of solute retained (or released) from the soil solution may be strongly time dependent. Selected examples of kinetic retention for Cd are given in Figure 2. Here, the kinetic dependence of Cd reactions, carried out in batch experiments, is shown for various soils (24). The amount of Cd retained varied among soils with Cecil soil exhibited the lowest retention, whereas the Sharkey soil showed maximum Cd retention. The sharp decrease in Cd concentrations indicates a fast-type sorption reaction, which was followed by slower type reactions. It is

also apparent that even after 300 hr, quasi-equilibrium conditions were not attained. The results shown in Figure 3 illustrate the influence of kinetic reactions on the shape of sorption isotherms of P in a Norwood soil. The amount of P sorbed increased with time as well as with concentration. It is apparent that the use of equilibrium-type models would yield inadequate predictions of the fate of such solutes in the soil system.

Several models have been proposed to describe the kinetic reactions of dissolved chemicals in the soil solution. Most common is the first-order kinetic reaction, which was incorporated into the convection-dispersion transport equation by Lapidus and Amundson (34). Such reactions are assumed to be fully reversible, and the magnitude of the reaction coefficients determines the time when apparent equilibrium may be attained. The use of such linear models has been rather restricted due to the nonlinear behavior of most solute retention reactions, exemplified by the cases shown in Figures 2 and 3. The first-order kinetic model has been modified to account for the nonlinear-kinetic behavior of retention mechanisms. Such a modified model was used successfully for describing the retention of P and several pesticides in batch and miscible displacement studies (16,35). Another fully reversible model is that of the Langmuir kinetic type (Table 2). Important features of this kinetic model are that it includes a maximum re-
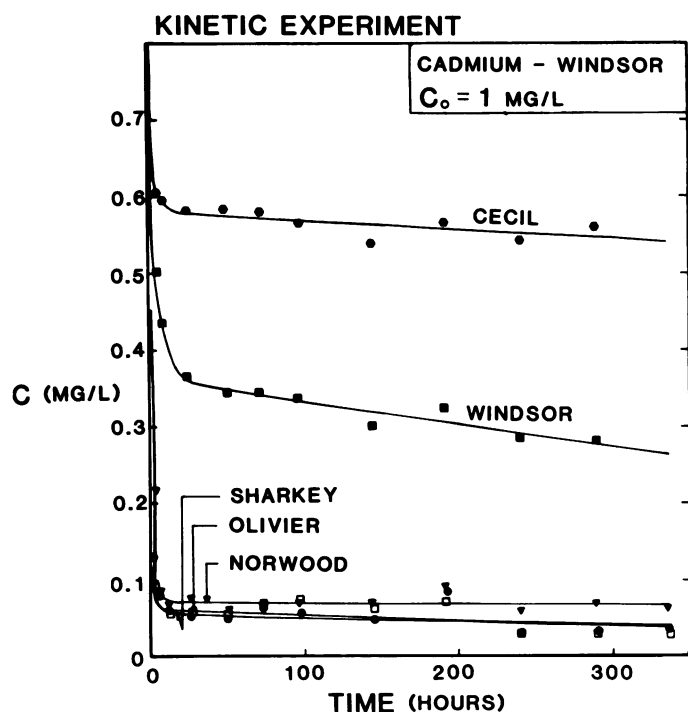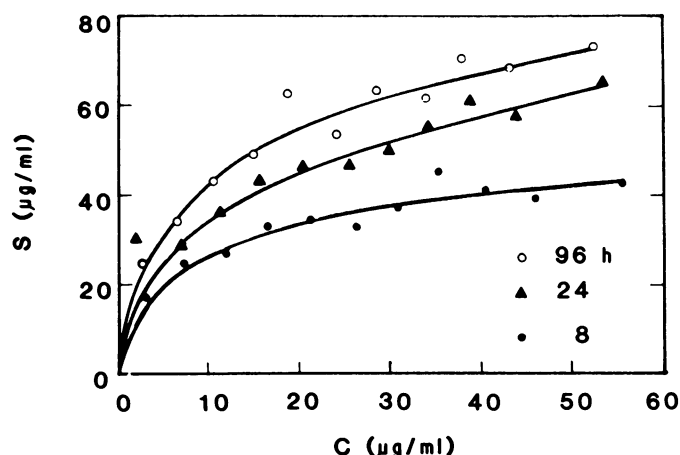

FIGURE 3. P sorption isotherms after 8, 24, and 96 hr of reaction time for a Norwood soil. Solid curves are predictions using the nonlinear Freundlich model.

Table 2. Insufficiently fast or kinetic-type models for contaminant retention in soils.

Model	Formulation
First-order	$\partial s/\partial t = k_1 (\Theta/\rho) c - k_2 s$
Nth order	$\partial s/\partial t = k_1 (\Theta/\rho) c^n - k_2 s$
Irreversible (sink/source)	$\partial s/\partial t = k_s (\Theta/\rho) (c - c_p)$
Langmuir kinetic	$\partial s/\partial t = k_1 (\Theta/\rho) c (s_{max} - s) - k_2 s$
Elovich	$\partial s/\partial t = A \exp(-Bs)$
Power	$\partial s/\partial t = k_1 (\Theta/\rho) c^n s^m$
Mass transfer	$\partial s/\partial t = k (\Theta/\rho) (c - c^*)$

FIGURE 2. Cd concentration vs. time of reaction for five soils (16).

tention capacity term and that it is nonlinear in nature (15). A discussion of the kinetic behavior of the Langmuir sorption reaction mechanisms during transport is presented by Jennings and Kirkner (36).

Multireaction Kinetic Models

A widely used multireaction model is the two-site model proposed by Selim et al. (37) and Cameron and Klute (38). This model was developed for the purpose of describing observed batch results, which showed rapid initial retention reactions followed by slower type reactions. The model was also developed to describe the excessive tailing of breakthrough results obtained from pulse inputs in miscible displacement experiments. Single retention models of the first and nth-order kinetic type failed consistently to describe such batch or miscible displacement results. The two-site model is based on several simplifying assumptions. It is assumed that a fraction of the total sites (referred to as type I sites) are highly kinetic in nature. As a result, type I sites were assumed to react slowly with the solute in the soil solution. In contrast, we consider type II sites to react rapidly with soil solution. The retention reactions for both types of sites were based on the nonlinear (or nth order) reversible kinetic approach as outlined in Table 2. The convention-dispersion transport equation with the two-site retention mechanism may be expressed as:

$$\Theta \frac{\partial c}{\partial t} = \Theta D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} - (k_1 \Theta c^n - k_2 \rho s_1)$$
$$- (k_3 \Theta c^m - k_4 \rho s_2) \tag{2}$$

$$\frac{\partial s_1}{\partial t} = k_1 \left[\frac{\Theta}{\rho}\right] c^n - k_2 s_1 \tag{3}$$

$$\frac{\partial s_2}{\partial t} = k_3 \left[\frac{\Theta}{\rho}\right] c^m - k_4 s_2 \tag{4}$$

$$s_t = s_1 + s_2 \tag{5}$$

where s_1 and s_2 are the amounts retained by sites I and sites II, respectively, and s_t is the total amount of solute retained. The nonlinear parameters m and n are usually considered less than unity and $n \neq m$. For the case $n = m = 1$, the retention reactions are of the first-order type, and the problem becomes a linear one. This two-site approach was also considered for the case when type II sites are assumed to be in equilibrium with the soil solution. Such conditions may be attained when the values for the forward and backward (or k_3 and k_4) rate coefficients are extremely large in comparison to the water flow velocity (q); that is, the local equilibrium assumption is valid for type II sites (39). Under these conditions, the solute convection-dispersion transport equation for a combined model of equilibrium and kinetic retentions is (37):

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - (k_1 c^n - k_2 \left[\frac{\rho}{\Theta}\right] s_1) \tag{6}$$

$$R = 1 + \left[\frac{\rho}{\Theta}\right] K_D m c^{m-1} \tag{7}$$

$$s_2 = K_D c \tag{8}$$

where Eqs. (7 and 9) describe equilibrium reaction of the Freundlich type. The term R of Eq. (7) is the retardation factor which for this nonlinear case is a function of c. Selim et al. (18) found that the use of the equilibrium and kinetic two-site model provided improved predictions of breakthrough curves (BTCs) for Picloram in soils. This result was due primarily to improved predictions of the excessive tailing of the desorption or leaching side and the sharp rise of the sorption side of the BTCs in comparison to predictions using single reaction equilibrium or kinetic models. Examples of predictions for two pesticides using this model are shown in Figure 4. Here, atrazine and (2,4-dichlorophenoxyacetic acid) were applied as separate pulses into different soil columns. The equilibrium and kinetic two-site model described in BTCs adequately for both pesticides and for different input pulse concentrations (c_0). In order to obtain the predictions shown in Figure 4, it was necessary that the retention reactions for the equilibrium and the kinetic sites were nonlinear with the values for m and n less than unity.

The two-site model has been used by several scientists including De Camargo et al. (40), Rao et al. (41), Hoffman and Rolston (42), Jardine et al. (43), Nkedi-Kizza et al. (8), and Parker and Jardine (44), among others. The model proved successful in describing the retention and transport of several dissolved chemicals, including aluminum, 2,4-D, atrazine, phosphorus, potassium, cadmium,, chromium, and methyl bromide.

Major disadvantages of the two-site model are that it is restricted to reversible mechanisms and that is does not account for possible consecutive-type solute interactions in the soil system. Several multireaction models have been introduced to incorporate irreversible as well as reversible reactions of the concurrent or the consecutive type. An example of a multireaction model is shown by the schematic diagram of Figure 5. Here we consider the solute to be present in the soil in five phases: c, s_1, s_2, s_3, and s_s. It is assumed that the rate of irreversible reaction ($\partial s_s/\partial t$), which is equivalent to the sink term Q of Eq. (1), can be expressed as

$$Q = \rho \frac{\partial s_s}{\partial t} = \Theta k_s c \tag{9}$$

This is a first-order irreversible kinetic process, and k_s is the associated rate coefficient (per day). Mansell et al. (35) proposed this approach for describing possible precipitation of P in miscible displacement studies. Fiskell et al. (45) found that incorporation of s_s in the model
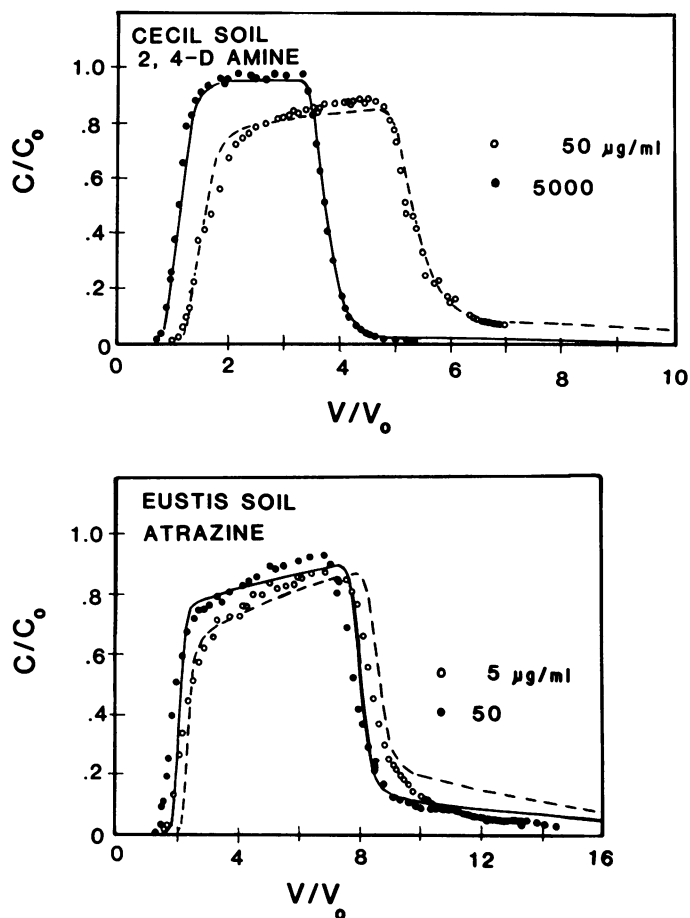
FIGURE 4. Breakthrough curves for 2,4-D amine and atrazine for two pulse concentrations. Dashed and solid curves are predictions using the two-site model (*21*).
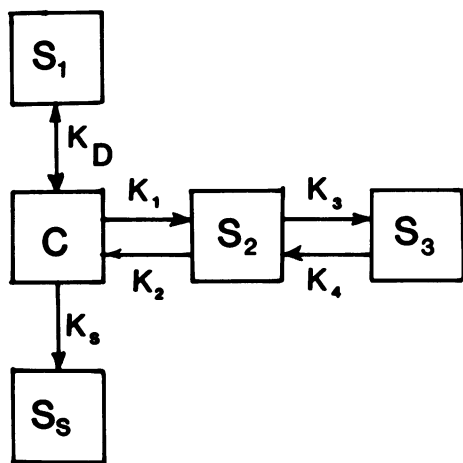
was essential in describing the slow P retention kinetics for a Spodosol from deep and shallow tilled treatments. Recently, Amacher et al. (*18*) showed that the sink term was necessary to describe batch results for Hg, Cd, and Cr retention versus time for five different soils. This sink term is similar to that for diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible and that k_s is related to the diffusion coefficient. Among kinetic models that are used to describe the rate of irreversible reactions is the Elovich model given in Table 2. For further discussion of irreversible kinetic models see Travis and Etnier (*16*).

As indicated by Figure 5, the s_1 and s_2 phases are in direct contact with c, and reversible processes of the equilibrium and kinetic types govern their reactions, respectively. The s_1 and s_2 phases may be regarded as the amounts adsorbed on surfaces of soil particles as well as chemically bound to Al and Fe oxides surfaces or other type surfaces. Moreover, these phases may be characterized by their fast sorption from, as well as release to, the soil solution and, thus susceptibility to leaching in the soil. In contrast, s_3 is considered here as the amount which is nonlabile, firmly held, or fixed by the soil matrix. Furthermore, this phase may be characterized by its slow (retention and release) reactions. Therefore, it is often assumed that the firmly held phase is less readily available to uptake by plant roots or transport in the soil profile.

The predictive capability of the multireaction model above was tested for two different solutes [P and Cr(VI)] and for various soils. As illustrated by the BTCs shown in Figures 6 and 7, the model is capable of describing the behavior of these solutes adequately. Such agreement may be regarded as adding credence to the validity of the model. For P predictions, we found that the presence of a consecutive reaction (or s_3) was necessary in order to describe the results shown. Moreover, the use of a simple first-order reaction to describe the

FIGURE 5. A schematic diagram of a multireaction model for solute retention in the soil system.
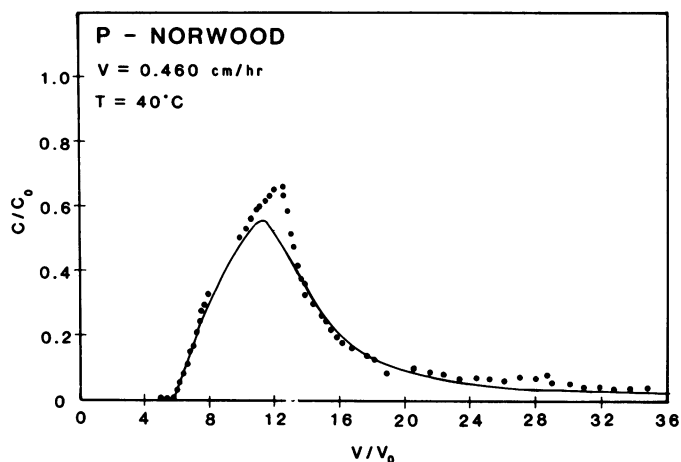

FIGURE 6. Breakthrough for P in a Norwood soil. Solid curve is the prediction using the multireaction model.
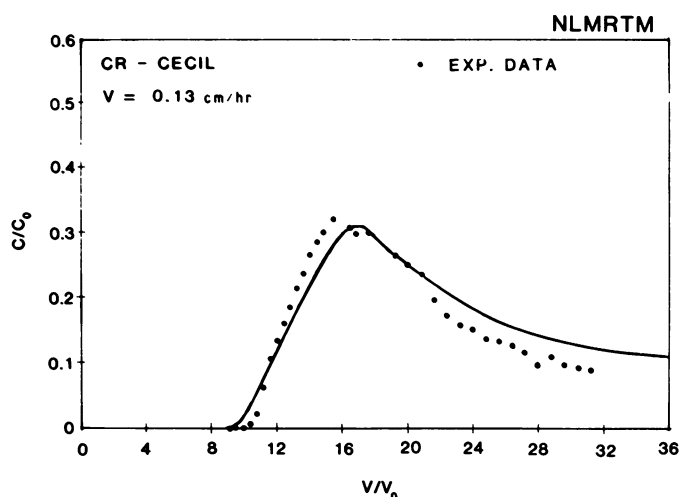
FIGURE 7. Breakthrough for Cr(VI) in a Cecil soil. Solid curve is the
prediction using the multireaction model.

slow kinetic retention of the consecutive type reaction
in the following form

$$\frac{\partial s_3}{\partial t} = k_3 \, s_2 - k_4 \, s_3 \tag{10}$$

proved to be adequate. Here, k_3 and k_4 are the asso-
ciated rates of reaction (per day). The model was equally
capable of describing BTCs for Cr(VI) and P from other
soils. Additional predictions were also obtained for
batch results (not shown) where a wide range of initial
concentrations were used in obtaining time-dependent
retention isotherms.

The multireaction model of Figure 5 may be regarded
as a simplified version of multicomponent models that
account for chemical and/or biological reactions of the
sequential and concurrent type. Examples of these re-
actions include precipitation/dissolution, mineralization,
immobilization, biological transformations, and radio-
active decay, among others. Models that account for
first-order kinetic decay reactions include those of Ras-
muson (6) and van Genuchten (46). Other examples of
this type of model are those that deal with soil nitrogen
transformations reactions (47). Other more complex
models are those that are based on ion-exchange reac-
tions for multiple ions along with chemical equilibrium
reactions in the soil solution. Examples of such models
include those of Jennings et al. (29), Miller and Benson
(30), and Cederberg et al. (32).

There are several advantages in using multireaction
models of the type shown in Figure 5. First, these
models are flexible and can be adapted to incorporate
other reactions of the reversible or irreversible type.
The governing reactions may be kinetic or equilibrium
in nature. Furthermore, such models are not restricted
to a specific number of solute species with either con-
current or consecutive reactions. However, a prereq-
uisite for the adoption of a multireaction model as a
predictive tool is that the model must be validated for
a specific contaminant and conditions under considera-

tion. To carry out complete validation of such a model
often requires extensive laboratory evaluation of nec-
essary model parameters. The dependence of model
parameters on other variables such as pH, temperature,
and redox potential must be determined. Moreover, it
is necessary that the model be evaluated for a range of
soils having different physical and chemical properties.
When rigorous validation of the model is not possible,
a partial validation based on a limited data set obtained
in the laboratory is necessary. Subsequent to laboratory
validation, the model should be tested with data sets
obtained from the controlled field experiments. Field
evaluation often results in several modifications of the
model. In some cases, it is perhaps desirable to have
more than one model version with each applicable for a
specified set of conditions. Although it is often recog-
nized that data sets that are suitable for model vali-
dation may not be available, it is essential that partial
model validation is performed.

Summary

An overview of several models that are used for the
description of the retention of dissolved chemicals dur-
ing transport in the soil profile is presented. Single re-
action models were classified into equilibrium and ki-
netic types. In addition, an equilibrium and kinetic two-
site model of the nonlinear type was presented. Major
advantages of this combination type model over the sin-
gle reaction approach were outlined and several solute
breakthrough curves illustrated. Furthermore, a gen-
eralized form of a multireaction kinetic model was given.
The major feature of multireaction kinetic models is that
they are flexible, being neither restricted by the number
of solute species present in the soil system nor by the
governing retention reaction mechanisms. Such models
may include reversible and irreversible reactions of the
linear and nonlinear kinetic types. Moreover, these
models can incorporate concurrent as well as consecu-
tive-type retention reactions that may be equilibrium
or kinetic in nature. Rigorous validation of such models
is needed for various contaminants and for soils having
different physical and chemical properties. Model vali-
dation is a prerequisite step before model adoption as
a predictive tool of the potential mobility of contami-
nants in soils.

REFERENCES

1. Brenner, H. The diffusion model of longitudinal mixing in beds
   of finite length, numerical values. Chem. Eng. Sci. 17: 220–243
   (1962).
2. Rao, P. S. C., Rolston, D. E., Jessup, R. E., and Davidson, J.
   M. Solute transport in aggregated porous media: theoretical and
   experimental evaluation. Soil Sci. Soc. Am. J. 44: 1139–1146
   (1980).

3. Rasmuson, A., and Neretienks, I. Exact solution of diffusion in particles and longitudinal dispersion in packed peds. J. Am. Inst. Chem. Eng. 26: 686–690 (1980).
4. Tang, D. H., Frind, E. O., and Sudicky, E. A. Contaminant transport in fracture porous media. Water Resources Res. 17: 555–564 (1981).
5. van Genuchten, M. Th., Tang, D. H., and Guennelon, R. Some exact and approximate solutions for solute transport through large cylinderical macropores. Water Resources Res. 20: 335–346 (1984).
6. Rasmuson, A. The effect of particles of variable size, shape and properties on the dynamics of fixed beds. Chem. Eng. Sci. 40: 621–629 (1985).
7. van Genuchten, M. Th., and Dalton, F. N. Models for simulating salt movement in aggregated field soils. Geoderma 38: 165–183 (1986).
8. Nkedi-Kizza, P., Biggar, J. W., Selim, H. M., van Genuchten, M. Th., Wierenga, P. J., Davidson, J. M., and Nielson, D. R. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated Oxisol. Water Resources Res. 20: 1123–1130 (1984).
9. Goltz, M. N., and Roberts, P. V. Interpreting organic solute transport data from a field experiment using physical nonequilibrium models. J. Contam. Hydrol. 1: 73–93 (1986).
10. Coats, K. H., and Smith, B. D. Dead-end pore volume and dispersion in porous media. Soc. Pet. Eng. 4: 73–84 (1964).
11. Skopp, J., and Warrick, A. W. A two-phase model for the miscible displacement of reactive solutes in soil. Soil Sci. Soc. Am. J. 38: 545–550 (1974).
12. van Genuchten, M. Th., and Wierenga, P. J. Mass transfer studies in sorbing porous media: I. Analytical solutions. Soil Sci. Soc. Am. J. 40: 473–480 (1976).
13. Skopp, J., Gardner, W. R., and Tyler, E. J. Solute movement in structured soils: two region model with small interactions. Soil Sci. Soc. Am. J. 45: 837–842 (1981).
14. Nielsen, D. R., van Genuchten, M. Th., and Biggar, J. M. Water flow and solute transport processes in the unsaturated zone. Water Resources Res. 22: 89S–108S (1986).
15. Rubin, J. Transport of reactive solutes in porous media: relation between mathematical nature of problem formulation and chemical nature of reactions. Water Resources Res. 9: 1231–1252 (1983).
16. Travis, C. C., and Etnier, E. L. A survey of sorption relationships for reactive solutes in soil. J. Environ. Qual. 10: 8–17 (1981).
17. Murali, V., and Aylmore, L. A. G. Competitive adsorption during solute transport in soils: 1. Mathematical models. Soil Sci. 135: 143–150 (1983).
18. Amacher, M. C., Kotuby-Amacher, J., Selim, H. M., and Iskandar, I. K. Retention and release of metals by soils—evaluation of several models. Geoderma 38: 131–154 (1986).
19. Reardon, E. J. K_d's—can they be used to describe reversible ion sorption reactions in contaminant migration? Ground Water 19: 279–286 (1981).
20. Larson, S. Soil phosphorus. Adv. Agron. 19: 151–211 (1967).
21. Fluhler, H., and Jury, W. A. Estimating Solute Transport Using Nonlinear Rate-Dependent Two-Site Sorption Model. Special Publ. No. 245, Swiss Federal Institute of Forestry Resources, 1983).
22. Holford, I. C. R., Wedderburn, R. W. M., and Mattingly, G. E. G. A Langmuir two-surface equation as a model of phosphate adsorption by soils. J. Soil Sci. 25: 242–254 (1974).
23. Schmitt, H. W., and Sticher, H. Long term trend analysis of heavy metal content and translocation in soils. Geoderma 38: 195–207 (1986).
24. Amacher, M. C., Selim, H. M., and Iskandar, I. K. Kinetics of chromium (VI) and cadmium retention in soils: a nonlinear multireaction model. Soil Sci. Soc. Am. J. 52: 398–408 (1988).
25. Veith, J. A., and Sposito, G. On the use of Langmiur equation in the interpretation of "adsorption" phenomena. Soil Soc. Am. J. 41: 697–702 (1977).
26. Sposito, G. On the use of Langmiur equation in the interpretation of "adsorption" phenomena: II. The "two-surface" Langmuir equation. Soil Sci. Soc. Am. J. 46: 1147–1152 (1982).
27. Rubin, J., and James, R. V. Dispersion-affected transport of reacting solution in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow. Water Resources Res. 9: 1332–1356 (1973).
28. Valocchi, A. J., Street, R. L., and Roberts, P. V. Transport of ion-exchanging solutes in groundwater: chromatographic theory and field simulation. Water Resources Res. 17: 1517–1527 (1981).
29. Jennings, A. A., Kirkner, D. J., and Theis, T. L. Multicomponent equilibrium chemistry in groundwater quality models. Water Resources Res. 18: 1089–1096 (1982).
30. Miller, C. W., and Benson, L. V. Simulation of solute transport in a chemically reactive heterogeneous system: model development and application. Water Resources Res. 19: 381–391 (1983).
31. Persaud, N., and Wierenga, P. J. A differential model for one-dimensional cation transport in discrete homoionic ion exchange media. Soil Sci. Soc. Am. J. 46: 482–490 (1982).
32. Cederberg, G. A., Street, R. L., and Leckie, J. O. A groundwater mass transport and equilibrium chemistry model for multicomponent systems. Water Resources Res. 21: 1095–1104 (1985).
33. Selim, H. M., Schulin, R., and Fluhler, H. Transport and ion exchange of calcium and magnesium in an aggregated soil. Soil Sci. Soc. Am. J. 51: 876–884 (1987).
34. Lapidus, L., and Amundson, N. L. Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic column. J. Phys. Chem. 56: 984–988 (1952).
35. Mansell, R. S., Selim, H. M. Kanchanasut, P., Davidson, J. M., and Fiskell, J. G. A. Experimental and simulated transport of phosphorus through sandy soils. Water Resources Res. 13: 189–194 (1977).
36. Jennings, A. A., and Kirkner, D. J. Instantaneous equilibrium approximation analysis. J. Hydrol. Div. Am. Soc. Civil Eng. 110: 1700–1717 (1984).
37. Selim, H. M., Davidson, J. M., and Mansell, R. S. Evaluation of a two-site adsorption-desorption model for describing solute transport in soils. Summer Computer Simulation Conference, Washington, DC, 1976, pp. 444–448.
38. Cameron, D., and Klute, A. Convective-dispersive solute transport with chemical equilibrium and kinetic adsorption model. Water Resources Res. 13: 183–188 (1977).
39. Valocchi, A. J. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. Water Resources Res. 21: 808–820 (1985).
40. De Camargo, O. A., Biggar, J. W., and Nielsen, D. R. Transport of inorganic phosphorus in an Alfisol. Soil Sci. Soc. Am. J. 43: 884–890 (1979).
41. Rao, R. S. C., Davidson, J. M., Jessup, R. E., and Selim, H. M. Evaluation of conceptual models for describing nonequilibrium adsorption-desorption of pesticides during steady flow in soils. Soil Sci. Soc. Am. J. 43: 22–28 (1979).
42. Hoffman, D. L., and Rolston, D. E. Transport of organic phosphate as affected by soil type. Soil Sci. Soc. Am. J. 44: 460–52 (1980).
43. Jardine, P. M., Parker, J. C., and Zelazny, L. W. Kinetics and mechanisms of aluminum adsorption on kaolinite using a two-site nonequilibrium transport model. Soil Sci. Soc. Am. J. 49: 867–873 (1985).
44. Parker, J. C., and Jardine, P. M. Effects of heterogeneous adsorption behavior on ion transport. Water Resources Res. 22: 1334–1340 (1986).
45. Fiskell, J. G. A., Mansell, R. S., Selim, H. M., and Martin, F. G. Kinetic behavior of phosphate sorption by acid, sandy soil. J. Environ. Qual. 8: 579–584 (1979).
46. van Genuchten, M.Th. Convective-dispersive transport of solutes involved in sequential first-order decay reactions. Comp. Geosci. 11: 129–147 (1985).
47. Iskandar, I. K., Ed. Modeling Wastewater Renovation. Land Treatment. John Wiley and Sons, New York, 1981.